BIOLIQUEFACTION OF COAL SYNTHESIS GAS

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INTRODUCTION

Synthesis gas, a mixture of primarily CO, H_2 and CO_2, is a major building block in the production of fuels and chemicals. The gas may be produced from several sources, including coal, oil shale, tar sands, heavy residues, biomass or natural gas. Most synthesis gas is produced today by catalytic reforming of natural gas, although the partial oxidation of heavy liquids is also practiced (1). Only a small percentage of the synthesis gas currently produced is by gasification of solid fuels. However, because of the large reserves of coal in the United States (300 year supply at the current consumption rate (2)), synthesis gas production from coal will become an important technology in the future.

CO, CO_2 and H_2 in synthesis gas may be used as substrates for the biological production of fuels and chemicals. The bacterium *Rhodospirillum rubrum* uses CO and water in producing H_2 and CO_2 (3,4). Bacteria such as *Peptostreptococcus productus* (5) and *Eubacterium limosum* (6) convert CO, CO_2 and H_2 to acetate. Butanol may be produced from CO using the bacterium *Butyribacterium methylotrophicum* (7) and ethanol may be produced from CO, CO_2 and H_2 by *Clostridium ljungdahlii* (8,9).

The anaerobic bacterium *C. ljungdahlii* produces ethanol and acetate from CO, CO_2 and H_2 by the equations (9):

$$6\ CO + 3\ H_2O \rightarrow C_2H_5OH + 4\ CO_2 \quad (1)$$

$$2\ CO_2 + 6\ H_2 \rightarrow C_2H_5OH + 3\ H_2O \quad (2)$$

$$4\ CO + 2\ H_2O \rightarrow CH_3COOH + 2\ CO_2 \quad (3)$$

$$2\ CO_2 + 4\ H_2 \rightarrow CH_3COOH + 2\ H_2O \quad (4)$$

The bacterium was isolated from animal waste, with the "wild" strain producing predominantly acetate in favor of ethanol. In fact, early studies showed an ethanol to acetate product ratio of 0.05 mol/mol and an ethanol concentration of less than 0.1 g/L (9). A major research effort was undertaken to improve the product ratio and increase the ethanol concentration. Studies at decreased pH (to 4.0) and with yeast extract removed from the liquid medium resulted in product ratios of 0.8 and an ethanol concentration of 1.8 g/L in the CSTR (10).

The purpose of this paper is to present results of continuous laboratory studies with *C. ljungdahlii* in converting CO, CO_2 and H_2 in synthesis gas to ethanol. In addition, the effects of the sulfur gas H_2S on growth and substrate uptake are presented and discussed.

MATERIALS AND METHODS

Clostridium ljungdahlii, Strain PETC, ATCC 49587, was originally ioslated from chicken waste in the University of Arkansas laboratories, and later identified and characterized by Dr. R. S. Tanner, University of Oklahoma, Department of Botany and Microbiology. The recommended medium for growth and ethanol production, as well as the techniques for handling the culture in batch and continuous reactors, have been presented previously (11,12).

RESULTS AND DISCUSSION

CSTR Performance

Growth and product formation in the CSTR are shown as a function of the inlet gas flow rate in Figures 1 and 2. The working liquid volume of the CSTR was approximately 350 mL, so that the minimum pseudo retention time on the figures was 30 min. The corresponding liquid retention time was 2.92 days. As is noted in Figure 1, the cell concentration remained nearly constant at about 1500 m/L for a gas flow rate range of 0.15 - 0.47 mmol/min. The ethanol concentration ranged from 15 to 22 g/L, increasing slightly with gas flow rate (see Figure 2). The corresponding acetate concentration ranged from 2 to 5 g/L. Thus, a maximum product ratio of 14.3 mole ethanol per mole acetate was obtained. This represents a dramatic shift from earlier studies where acetate was the predominant product and low product concentrations were obtained. The specific production rate, calculated as the moles of products (both ethanol and acetate) produced per g cell per hour, was essentially constant at 0.004 regardless of gas flow rate.

Studies were also carried out with *C. ljungdahlii* in a CSTR with cell recycle. In this study, the liquid volume was 1000 mL, the temperature was 36°C and the pH was held constant at 4.5. The agitation rate was increased from 300 to 450 rpm and the gas flow rate was increased from 10 to 30 mL/min during the study to accomodate cell growth in the reactor. The liquid flow rate to the cell recycle reactor was 3.5 to 12 mL/h, decreasing with time of operation.

Figure 3 presents cell concentration measurements for the CSTR with cell recycle. As is noted, the cell concentration increased (with agitation rate and gas flow rate increases) from approximately 800 mg/L to over 4000 mg/L. The maximum in the previous CSTR study without cell recycle (see Figure 1) was 1500 g/L. The CO conversion, shown in Figure 4, hovered around the 90 percent level after 150 h of operation. The corresponding H_2 conversion, on the other hand, averaged 70 percent up to a time of 500 h. At this time, the H_2 conversion fell, probably due to an accumulation of CO in the liquid phase. It is likely that a growth limitation by a liquid constituent prompted a drop in CO conversion, resulting in CO build-up in the liquid phase and CO inhibition.

Product concentration measurements during the study are shown in Figure 5. The ethanol concentration ranged from 6 g/L at the beginning of the study to 48 g/L after 560 h of operation. The corresponding acetate concentrations at these times were 5 g/L and 3 g/L, respectively. The ratio of ethanol to acetate ranged from 1.6 mol/mol to 21 mol/mol. Thus, very high ethanol concentrations are possible with favorable product ratios.

Sulfur Gas Tolerance of *C. ljungdahlii*

Many bacterial cultures capable of converting CO to products have been found to be quite tolerant of the sulfur gases H_2S and COS (13,14). *Peptostreptococcus productus*, for example, which converts CO to acetate, is able to successfully convert CO to acetate in the presence of 19.7 percent H_2S or COS after culture acclimation. The methanogen *Methanobacterium formicicum*, on the other hand, is able to tolerate only 6.6 percent H_2S or COS. However, even this latter result is encouraging, since typical coal-derived synthesis gas contains only 1-2 percent sulfur gases, mainly as H_2S.

C. ljungdahlii, grown in the presence of Na_2S in place of cysteine-HCl as the reducing agent for several weeks, was evaluated for its tolerance to H_2S in batch bottle experiments. The 155 mL bottles containing 50 mL of liquid medium devoid of yeast extract and adjusted to pH 4.3, were first gassed with synthesis gas to a pressure of 10.7 psig. The desired amount of H_2S or COS (2.5 mL-20 mL) at 1 atm was then added. This batch system was allowed to equilibrate overnight. As a final step, 10 mL of *C. ljungdahlii* were added prior to incubation at 34°C.

The effects of H_2S on growth and substrate uptake by *C. ljungdahlii* are shown in Figures 6 and 7, respectively. As is noted in Figure 6, growth was not significantly slowed at H_2S concentrations below 5.2 percent. Upon the addition of 9.9 percent H_2S, however, growth essentially stopped. Similar results are noted with substrate uptake in the presence of H_2S (see Figure 7). The presence of H_2S slowed the rates of substrate uptake only slightly up to an H_2S concentration at 5.2 mole percent. Similar results were obtained with concentrations of COS up to 5.2 percent.

These concentrations are far in excess of maximum sulfur gas concentrations possible in coal synthesis gas. It should also be realized that dramatic effects can be obtained with prolonged sulfur gas acclimation. *P. productus*, for example, was only marginally tolerant of H_2S and COS in initial studies. Concentrations up to 20 percent were tolerated after a period of acclimation to the sulfur gases.

CONCLUSIONS

Clostridium ljungdahlii was shown to grow on synthesis gas with the production of high concentrations of ethanol and acetic acid. The relative amounts of ethanol and acetate can be controlled by nutritional factors, substrate gas supply, and pH. Low pH (4.0 to 4.5), high mass transfer of an adequate supply of substrate gas, and minimal medium all favor ethanol production. A CSTR cell recycle system has been shown to be effective in permitting the cell concentrations necessary for high concentrations of ethanol. An ethanol concentration of 47 g/L with a corresponding acetate of 2 g/L has been attained. Finally, *C. ljungdahlii* has been shown to be tolerant of H_2S or COS in concentrations exceeding typical levels in synthesis gas.

ACKNOWLEDGMENT

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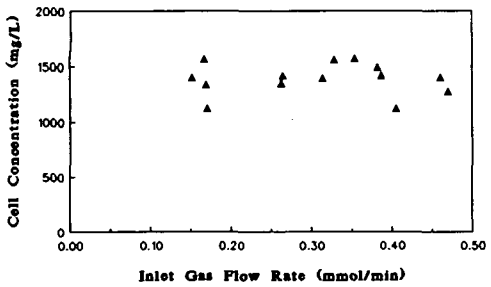

Figure 1. Cell Concentrations Obtained in the CSTR

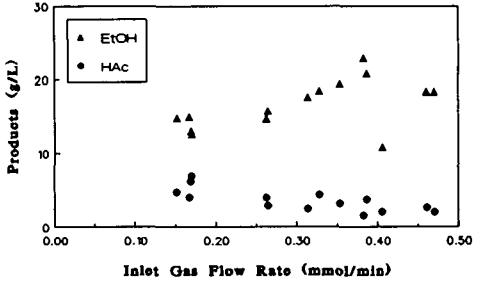

Figure 2. Product Concentrations Obtained in the CSTR

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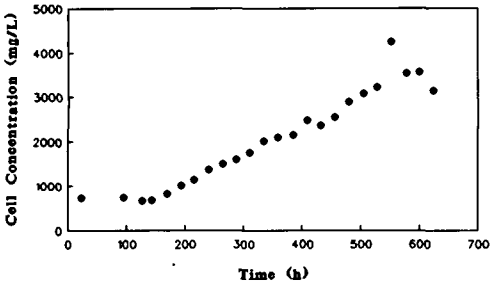

Figure 3. Cell Concentration Measurements in the CSTR with Cell Recycle

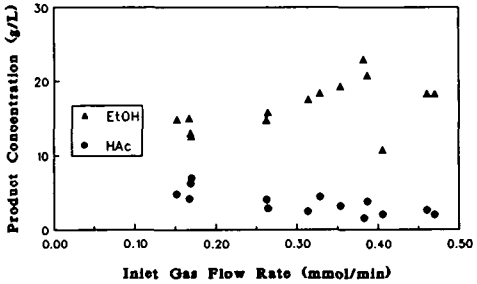

Figure 4. CO and H_2 Conversions in the CSTR with Cell Recycle

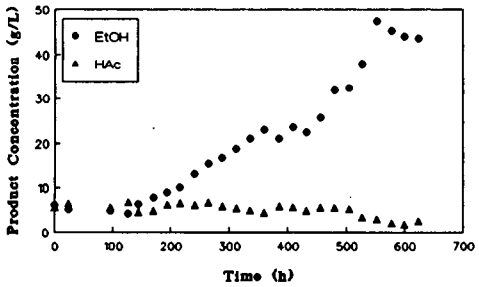

Figure 5. Product Concentration Measurements in the CSTR with Cell Recycle

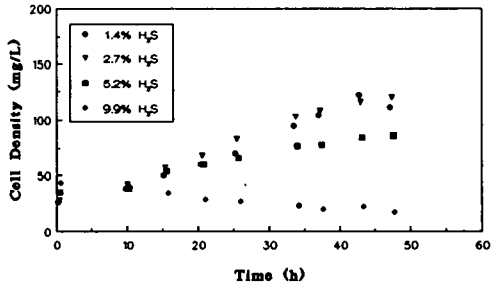

Figure 6. Effects of H_2S on the Growth of *C. ljungdahlii* in Batch Culture

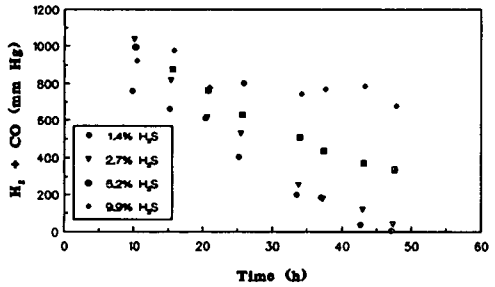

Figure 7. Effects of H_2S on CO and H_2 Uptake by *C. ljungdahlii* in Batch Culture